

RESEARCH ARTICLE

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Key Points:

- Under certain eruptive and atmospheric conditions, Icelandic tephra particles can reach European glaciers
- Geochemical composition of tephra particles extracted from a recent expedition's ice core drilling chips point to a single volcanic source
- Timing and chemistry of particles points to massive nineteenth century eruption in Eastern Iceland that deposited tephra layers in Europe

Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2
- Data Set S3
- Data Set S4
- Data Set S5
- Data Set S6
- Data Set S7
- Data Set S8
- Data Set S9
- Data Set S10
- Data Set S11

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Possible Icelandic Tephra Found in European Colle Gnifetti Glacier

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Abstract Volcanic ash (tephra) provides unique time markers (isochrons) that are often used as an independent age-control tool for stratigraphic correlations of paleoclimate archives from ice cores. However, little credence has been given to the notion of finding tephra in ice cores collected in the European Alps because of the relatively large distance from volcanic sources and the presumed nature of regional atmospheric circulation patterns. We filtered particles from melted ice core drilling chips gathered roughly every meter during a 2013 drilling operation at Colle Gnifetti glacier in the Swiss-Italian Alps (45°55.74'N, 7°52.58'E, 4450 m asl). One filter, preliminarily dated to the nineteenth century by annual layer counting, contained a group of six visually similar tephra particles. Analyzing their chemistry using a scanning electron microscope equipped with an energy-dispersive x-ray spectrometer established that the six particles were volcanic in origin and are very similar in composition (a distinctive geochemical signature), pointing to a single volcanic eruption source. We proposed that one of several massive nineteenth century Eastern Icelandic eruptions is a potential source given eruption timing, size, tephra dispersion area, and similarities in chemical composition. This first finding of tephra in an Alpine ice core contributes to a regional tephrochronological framework that can be adapted for future correlation among different paleoclimate sequences.

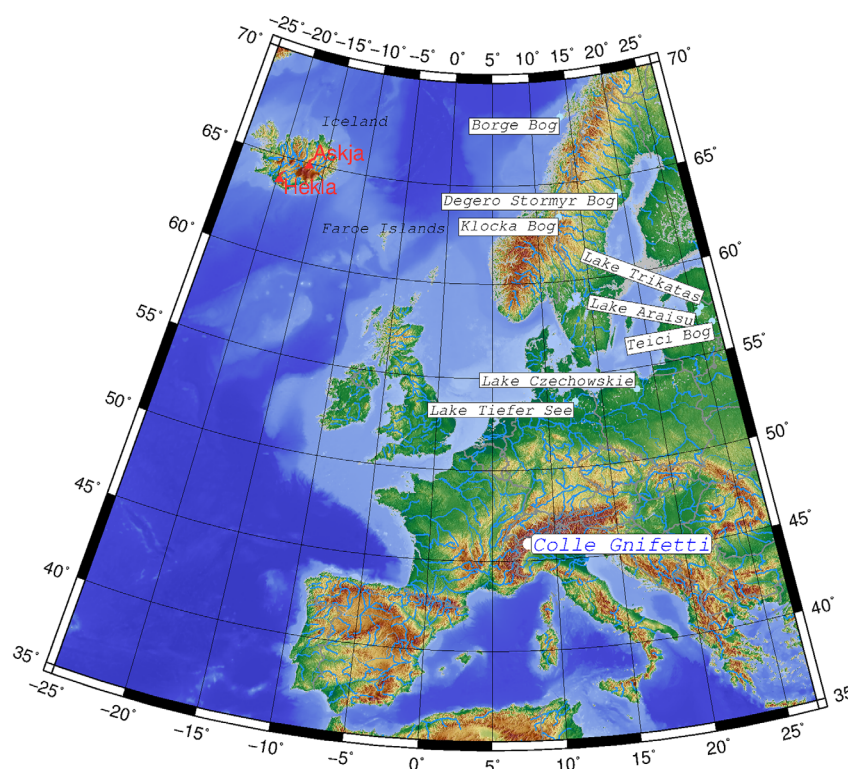
1. Introduction

Volcanic ash (tephra) from large, explosive volcanic eruptions very rapidly spreads over large areas and creates a unique time marker that can be used to synchronize and inform stratigraphic time series (Lowe, 2011). Through a careful study of composition and chemistry, identified tephra (see foundation of tephrochronological method in Thorarinsson, 1981a, 1981b) allow regional paleoclimate archives to be independently correlated (Wulf et al., 2016). Tephrochronology is a tool often used to verify constructed time scales of ice core time series and other paleoclimate reconstructions by providing absolute dating tie-points which are independent of derived ice core ages.

Located in the Swiss-Italian Alps, the Colle Gnifetti glacier (Figure 1) is one of the small number of ice core drilling sites in the European Alps offering preserved paleoclimate records over the last millennium and potentially beyond (More et al., 2017; Schwikowski, 2004; Wagenbach et al., 2012). A recent drilling expedition to Colle Gnifetti yielded an ice core from this glacier, which is the focus of another study that connected ice core based reconstructions of climate with historical archives (More et al., 2017). Developing a robust time scale that uses several independent dating methods for increased accuracy is crucial for future studies with this ice core.

Due to the low and irregular net snow accumulation and rapid layer thinning, employing traditional dating methods such as annual layer counting in cm-resolution impurity profiles is typically limited to a few hundred years at Colle Gnifetti (Bohleber et al., 2013). Age constraints for Colle Gnifetti ice cores can also come from three-dimensional ice flow modeling (Lüthi & Funk, 2000; Wagner, 1996) combined with radiocarbon dating (Hoffmann, 2016; Jenk et al., 2009; May, 2009).

Identification of compounds from volcanic eruptions of known ages is often accomplished using sulfate or other volcanically produced chemical species preserved in the ice core chemistry record. This technique is employed successfully on polar ice cores (e.g., Hammer, 1977), but is fundamentally hampered at Colle



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Figure 1. Location of the Colle Gnifetti ice core (white dot), Askja & Hekla volcanoes (red triangles), and lake core/bog sites (blue circles) where tephra from the 1875 C.E. Askja event has been identified (Bergman et al., 2004; Lind & Wastegård, 2011; Pilcher et al., 2005; Stivrins et al., 2016; Watson et al., 2016; Wulf et al., 2016).

Gnifetti due to frequent influxes of Saharan dust that contribute substantially to overall sulfate background concentrations (Wagenbach & Geis, 1989; Wagenbach et al., 1996), confounding any potential sulfate increases due to volcanic sources. Potentially less ambiguous in this respect would be the direct detection of tephra.

Some skepticism regarding the possibility of finding tephra in European Alpine ice cores exists because of assumptions concerning regional atmospheric circulation patterns and the relatively large distance from active volcanic sources to, in our case, the Colle Gnifetti site. Out of the almost dozen ice cores collected in the European Alps, not a single tephra layer has been identified. However, there are many documented instances of tephra, especially from Iceland, reaching mainland Europe throughout the last 10,000 years (Barber et al., 2008; Carey et al., 2010; Dugmore, 1989; Dugmore et al., 1995; Lane et al., 2011; Lind & Wastegård, 2011; Mohn, 1878; Persson, 1971; Stevenson et al., 2012; Wastegård, 2002, 2005; Wastegård & Davies, 2009; Wulf et al., 2013, 2016). The last volcanic cloud from Iceland reached Europe as recently as 2010 (Stevenson et al., 2012), but tephra from this moderate volcanic event didn't create a distinct depositional layer. Considering the abundance of Icelandic tephra and cryptotephra discovered in proximity to the study area, we hypothesize that very fine-grained insoluble material from at least the largest Icelandic eruptions (labeled 'cryptotephra' by Lowe & Hunt, 2001) could be transported to Colle Gnifetti under rapid direct atmospheric transport scenarios. Supporting information Table S1 lists the largest volcanic eruptions of the nineteenth century, those with a Volcanic Explosivity Index (VEI) ≥ 4 (data compiled by the *Smithsonian Institution Global Volcanism Project* (Global Volcanism Program, 2013) using criteria developed by Newhall & Self, 1982).

2. Materials and Methods

In this study we relied on the so-called "drilling chips" collected roughly every meter during ice core recovery. At the sampling interval discussed in this paper, a meter of the ice core corresponded roughly to five decades. The ice core time scale was developed by counting annual layers represented in the sharp

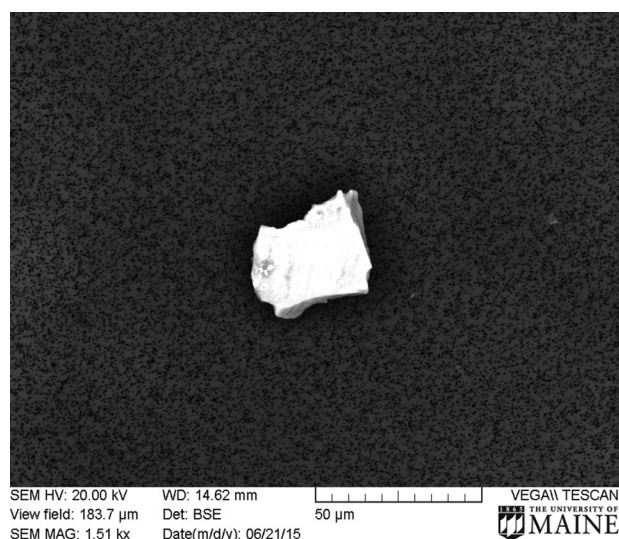


Figure 2. Image of one of the six cryptotephra particles from the 2013 ice core at Colle Gnifetti captured by SEM-EDS.

summer-winter contrast of impurity concentrations. A sub-cm-resolution of the ice chemistry profiles (including NH_4^+ and Ca^{2+}) was achieved from continuous melting of the ice core, and on an ultra-high resolution LA-ICP-MS Ca-profile where annual layers are not resolved by the continuous melting data due to the progressive thinning of the layers with depth (Bohleber et al., 2013; Kaufmann et al., 2008; Sneed et al., 2015). These measurements were combined with inline and discrete measurements. All insoluble particles were filtered from the meltwater from the chips of the respective drilling run. A 0.4 micron poly-carbonate membrane filtering system offers a well-established technique successively used for ice core tephra sampling (Dunbar et al., 2003; Palais et al., 1987).

We examined twenty filters at the University of Maine's micro-beam laboratory using a scanning electron microscope *Tescan Vega-II XMU* variable pressure instrument equipped with an EDAX Pegasus integrated energy-dispersive spectrometry (SEM-EDS). While scanning and searching through the filters, we looked for particles typical of the shape of volcanic glass (Figure 2). Due to the small size of the particles (several microns across), the flat surface polishing required for wavelength-dispersive x-ray spectrometry (WDS) was not a viable option. Instead when a suspected cryptotephra particle was discovered, EDS

spectral data were collected on the particles captured on the surface of the filtering material (see method details in Iverson et al., 2016).

3. Data

One filter, containing insoluble material gathered from the 2013 ice core at the depth of 41.575–42.410 m and dated (Bohleber et al., 2017) to the nineteenth century based on layer-counting, contained a group of six visually similar candidate particles. The distinctive chemistry of the six particles examined (Table 1) allowed us to conclude that the shared geochemical signature pointed to volcanic glass composition from a single volcanic source.

4. Results

Of the forty-five large ($\text{VEI} \geq 4$) nineteenth century volcanic eruptions listed in supporting information Table S1, (Global Volcanism Program, 2013) forty eruptions did not occur in the same hemisphere as Colle

Table 1
Chemistry of Six Cryptotephra Particles Collected From 2013 Colle Gnifetti Ice Core

Sample ID	SiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
3.0A	76.19	13.44	1.09	0.09	0.21	0.79	5.19	2.60	0.30	0.11
Run 45-9										
3.0A	76.19	13.44	1.09	0.09	0.21	0.79	5.19	2.60	0.30	0.11
Run 45-10										
3.0A	75.27	13.86	1.47	0.10	0.19	0.83	5.46	2.42	0.28	0.11
Run 45-12										
3.0A	76.23	13.16	1.37	0.07	0.27	0.96	4.62	2.76	0.29	0.26
Run 45-15										
3.0A	76.77	13.12	1.53	0.09	0.38	1.13	2.82	3.72	0.43	0.00
Run 45-16										
3.0A	74.62	14.91	1.33	0.09	0.37	0.94	4.16	3.15	0.42	0.00
Run 45-19										
Mean	75.9	13.70	1.30	0.10	0.30	0.90	4.60	2.90	0.30	0.10
1 std.	0.80	0.70	0.20	0.01	0.10	0.10	1.00	0.50	0.10	0.10
Method Uncertainty (%) ^a	0.60	0.12	0.05	0.01	0.02	0.40	0.40	0.06	0.08	0.08

Note: Mean and one standard deviation uncertainty are also included. Analytical errors were determined from repeated measurements of a Rhyolite NMNH 72854 VG-568 standard.

^aCalculated from repeated analysis of standard glass during the same session as when analyses were performed.

Gnifetti and so were disregarded as likely sources in this study. Two of the five remaining volcanic eruptions, the 1845 C.E. Hekla and 1875 C.E. Askja events, both in Eastern Iceland but with distinctively different geochemical signatures, were large enough that ash fall was reported in continental Europe and tephra from each eruption has been found in European lake and peat cores (Wastegård, 2002, 2005; Wastegård & Davies, 2009; Wulf et al., 2013, 2016). Additionally, as cryptotephra studies developed, it became apparent that even comparatively small scale silicic eruptions could spread cryptotephra over very long distances (Boygles, 1998; Dugmore et al., 1996). We therefore focused on the 1845 C.E. Hekla and 1875 C.E. Askja eruptions as possible candidates for the source of the particles found in the Colle Gnifetti ice core.

A comparison of the chemistry of the six candidate particles with published Askja-S, 1875 C.E. Askja, and 1845 C.E. Hekla tephra chemistry gathered from WDS-equipped microprobe analyses (Bergman et al., 2004; Lind & Wastegård, 2011; Macdonald et al., 1987; Sparks et al., 1981; Stivrins et al., 2016; Wastegård, 2002; Wulf et al., 2016) shows reasonable concurrence (Figure 3) within the $\pm 2\%$ uncertainty on the SEM-EDS derived chemical composition. The comparison of data gathered by EDS with data gathered by WDS normally should not affect results and should allow for accurate comparison when samples are large (Grönvold et al., 1995). In our case, however, small sample size could potentially greatly influence our results, but we obtained compatible measurements on another tephra layer detected in an Antarctic ice core (Koffman et al., 2017).

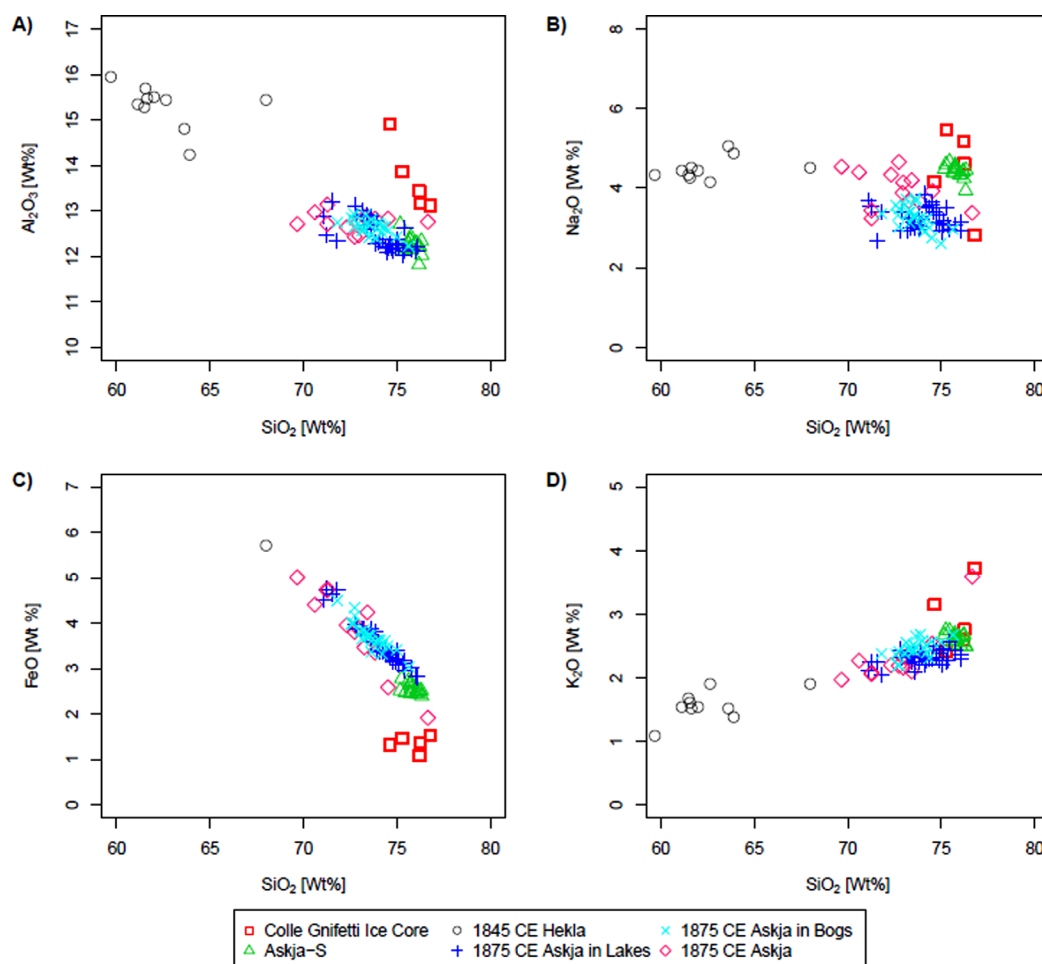


Figure 3. Composition of cryptotephra particles (red squares) from 41.575 to 42.41 m interval in 2013 Colle Gnifetti ice core compared to tephra glass compositions from the early Holocene Askja-S (green triangles: Lind & Wastegård, 2011), 1875 C.E. Askja in lakes (blue crosses: Stivrins et al., 2016; Wulf et al., 2016), bogs (teal crosses: Bergman et al., 2004; Stivrins et al., 2016), and at the Askja crater (pink diamonds: Macdonald et al., 1987; Sparks et al., 1981), and 1845 C.E. Hekla (black circles: Wastegård, 2002). All analyses are normalized and recalculated to 100% for SiO₂, Al₂O₃, FeO, Na₂O, K₂O, MnO, MgO, CaO, Ti₂O₃, & P₂O₅ oxides.

Previous studies, such as Dugmore et al. (1992), show that in the absence of absolute precision, chemistry still provides compelling evidence for identification and correlation of cryptotephra, especially when used in combination with other evidence. Considering the timeline inferred from the Colle Gnifetti ice core and assuming a very conservative time scale uncertainty (± 25 years), the 1875 C.E. Askja eruption is the most likely candidate of all potential tephra from Iceland or the Mediterranean with similarly high silica values during this time frame. The only other possible eruption with such a high silica content is the Minoan eruption of Thera in Santorini in the mid-second millennium B.C.E. (Eastwood et al., 1999). Additionally, the 1875 C.E. Askja eruption dispersed up to 0.3 km^3 of tephra clouds into the atmosphere (Hartley et al., 2016), and tephra deposits from this eruption were found in a number of neighboring sites (Figure 1).

5. Conclusions

Although a solely geochemistry-based match of the six particles in the ice core with the composition of the 1875 C.E. Askja eruption cannot be definitive due to large uncertainties (up to 2% in some elements) in the employed EDS method as a result of the small particle sizes (Iverson et al., 2016), the close chemical composition and tephra presence in vicinity of the drill site cumulatively point to the fact that the six Colle Gnifetti particles are tephra, likely from Eastern Iceland.

This pilot study also demonstrates the feasibility of finding cryptotephra that can be used to constrain an annual layer depth/age chronology from Colle Gnifetti area ice cores. In future studies, we encourage integrating tephra sampling with the ice core measurements and allocating sufficient ice volume for success in sampling.

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